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(54) Title: UV-CURABLE COMPOSITIONS COMPRISING AN ACYL PHOSPHINE OXIDE AND AN OPTICAL BRIGHTENER

(57) Abstract

A photocurable composition comprising at least one ethylenically unsaturated compound, an acylphosphine oxide initiator, as a photosensitiser, an optical brightener. The photocurable compositions have utility in photoimaging systems e.g. color proofing systems.

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UV-CURABLE COMPOSITIONS COMPRISING AN ACYL PHOSPHINE OXIDE AND AN OPTICAL BRIGHTENER

The invention relates to UV-curable compositions comprising, as photoinitiator, the combination of an acylphosphine oxide and an optical brightener. The compositions are useful in the field of radiation curable coatings in general, and in particular are useful in the field of photoimaging, especially color proofing.

Photocurable compositions are well known, and find use in areas as diverse as protective coatings (clear or pigmented), photoimaging systems and printing inks. Such compositions typically comprise one or more photoinitiators and one or more compounds possessing an unsaturated group susceptible to free-radical polymerisation. The photoinitiator is a compound which generates free radicals in response to absorption of radiation, typically near UV radiation in the wavelength range 340 to 400 nm, or by interaction with a photoexcited sensitizer, the resulting radicals initiating the polymerisation of the polymerizable compound(s). Generally, the polymerizable compounds possess two or more unsaturated groups per molecule so that a rapid increase in molecular weight, and formation of a cross-linked network, are the net effects of photoirradiation. This provides the necessary structural integrity and durability in the case of protective coatings. In the case of photoimaged materials, the pattern of high and low molecular weight media (cross linked and uncrosslinked) resulting from an imagewise exposure produces differences in physico-chemical properties which may be processed in a variety of ways to provide a useful image. For example, unexposed regions may be selectively dissolved out by a suitable developing fluid, as in photoresist technology, which is used in the production of printing plates, semiconductor masks, printed circuit boards, color proofs, and the like. As an alternative to wet development, an imagewise exposed layer of photocurable material may be subjected to peel-apart processing, in which the layer, initially sandwiched between two substrates, is partitioned between the substrates when they are peeled apart. Alternatively, colored toner may be adhered

selectively to unexposed areas by virtue of their greater tackiness, giving a colored image useful for color proofing purposes. These (and other) imaging processes based on photopolymerisation are described in greater detail in references such as, "Imaging Processes and Materials" (Neblette's 8th Edition), ed. Sturge et al, chapter 7, pp 226-262 (Van Nostrand, 1989).

There is a continuing interest in improving the sensitivity of photocurable systems, i.e. the degree of polymerisation or crosslinking obtainable from an exposure of given intensity and duration. This is directly related to the efficiency of light capture, i.e. the proportion of the incident light which is actually absorbed by the photocurable medium. Regardless of how efficient the polymerisation process itself may be, if only a small proportion of the incident energy is utilised, the overall efficiency will be low.

The simplest method of increasing the efficiency of light capture is to increase the concentration of the species responsible for absorbing the light, namely the photoinitiator and/or the photosensitizer. However, this will frequently result in a visible coloration (yellowing) of the medium, which is unacceptable for many applications such as clear protective coatings, color proofing elements, etc. Because the most commonly used light source is a UV lamp emitting in the 340 to 380 nm range, photoinitiators and/or photosensitizers typically exhibit an absorption maximum in the same range. However, the relevant absorption bands are relatively broad, and generally have a "tail" extending into the visible region (> 400 nm), so that as the concentration of the relevant compounds increases, the "tail" gives rise to a visible yellow coloration. There is therefore a compromise between sensitivity and acceptable appearance of the final coating or image.

In the case of imaging media comprising photocurable compositions, there is a further reason why highly efficient light capture is desirable, namely the suppression of halation. Halation arises when light passes through a layer of a photocurable medium, strikes the surface of the substrate on which the layer is coated, and reflects back into the layer, where it is absorbed and may initiate photocuring. If the substrate is diffusely-reflecting, the reflected light may enter areas of the coating that were not intended to be exposed, leading to photocuring in a wider area than was

originally intended, and hence a loss of resolution. The problem can be solved by ensuring that the coating absorbs enough of the exposing radiation so that the proportion of reflected light is insufficient to cause a significant degree of curing. The incorporation in the coating of inert UV absorbers (known as acutance dyes) is well known in the art of photoimaging as a means of alleviating the halation problem. However, this generally leads to a reduction in sensitivity due to competition between the acutance dye and the initiator for the exposing light, and can also give rise to the yellowing problem described above, so that there will be a compromise among sensitivity, resolution and cosmetic appearance. This problem is particularly severe in the field of color proofing, where exposure typically takes place against a white, diffusely-reflecting base, resolution demands are high, and tolerance of yellowing is low.

Acylphosphine oxides are a class of photoinitiator disclosed in US Patent No. 4,265,723. The class has found increasing use in the protective coatings industry, but has not found widespread use in photoimaging. The relevant compounds have an absorption maximum at around 380 nm which provides a good match with conventional UV sources, and absorbed light is converted to initiating radicals with high efficiency. However, the molar extinction coefficient (and hence the efficiency of light capture) is comparatively low. This combination of properties is useful in the field of surface coatings, where low residual color and/or curing to a depth of several millimetres may be important, and where multiple passes through the exposing station are possible. (See, for example, "Radiation Curing of Polymers II" (Royal Society of Chemistry Special Publication No. 89) pp 109-111). In the case of photoimaging, however, the low efficiency of light capture is seen as a severe disadvantage.

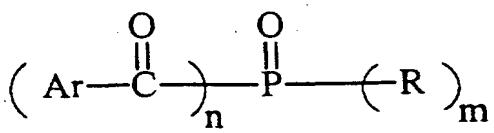
US Patent No. 5,210,110 and WO96/07662 disclose particular classes of acylphosphine oxide initiators, and further disclose that their spectral sensitivity may be shifted or broadened by the addition of photosensitizers which are aromatic carbonyl compounds, such as derivatives of benzophenone, thioxanthone, anthraquinone and 3-acylcoumarins.

Optical brighteners (also known as fluorescent brighteners, optical whiteners or fluorescent whiteners) are a known class of compounds disclosed, for example, in standard reference works such as Kirk-Othmer's Encyclopedia of Chemical Technology, 4th Ed., Vol. 11, pp.227 - 241. The relevant compounds are characterised by an intense absorption in the near UV region of the spectrum and a correspondingly intense fluorescence in the blue region. Thus, they have the useful property of counteracting any yellowing that may occur in articles or compositions that are intended to appear colorless or pure white, and find widespread use in fields such as textiles, paper, artificial fibres and detergents. Optical brighteners have also been used in color proofing media to mask the yellowing effects of excess initiator, sensitizer etc., which would otherwise corrupt the fidelity of the color reproduction. US Patent No. 3,854,950 discloses the use of substantial quantities of optical brighteners (sufficient to attenuate incident light by at least 50%) in photohardenable compositions useful in the formation of color proofs via toning with colorants. The stated objective is to minimise halation effects without introducing background stain.

According to the present invention, there is provided a photocurable composition comprising at least one ethylenically unsaturated compound, an acylphosphine oxide initiator, and an optical brightener that functions as a photosensitizer.

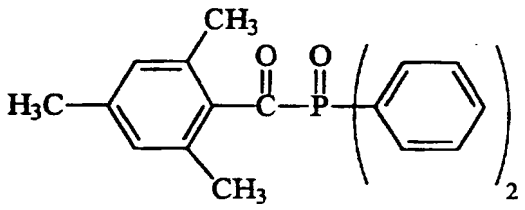
In another embodiment of the invention, a photoimageable element is provided comprising a coating of the above composition on a substrate and a method for imaging the element.

Suitable acylphosphine oxide initiators for use in the invention are disclosed in US Patent No. 4,265,723. Preferred acylphosphine oxides have a nucleus of formula

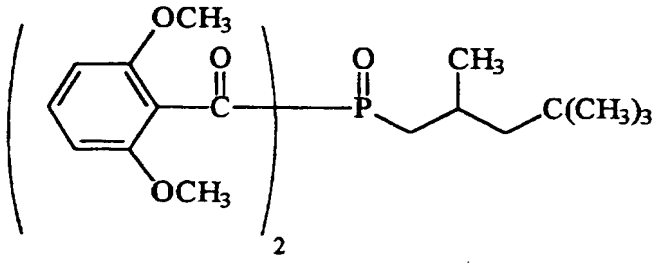


in which: n and m are 1 or 2 such that (n + m) = 3; Ar represents an aryl or heteroaryl group which groups generally contain up to skeletal 12 atoms selected from C, N, O, S and P; and each R is independently selected from alkyl, cycloalkyl, aryl and heterocyclic groups, which groups generally contain up to skeletal 12 atoms selected from C, N, O, S and P, or when m = 2 both R groups may together complete a cyclic structure comprising atoms selected from C,N,O,S and P.

Any of the groups represented by Ar or R may bear one or more additional substituents, provided such substituents do not interfere with the photocuring process or impart a visible coloration before or after photocuring. Suitable substituents include alkyl, alkoxy, hydroxyl, alkoxycarbonyl etc. Preferred acylphosphine oxide initiators include the following compounds (1) and (2).



(1)



(2)

Compound (1) is available from Ciba-Geigy under the tradename Lucirin TPO. Optionally, initiators of other classes, such as benzophenones, acyloins, benzils etc., may be present in addition to the acylphosphine oxide initiator. For example, Darocur™ 4265 is a commercially available mixture (supplied by Ciba-Geigy) comprising equal weights of Compound (1) and 2-hydroxy-2-methylphenylpropan-1-one and is suitable for use in the invention. Similarly, Irgacure™ 1700, available from Ciba-Geigy, is a mixture comprising 25 wt% compound (2) and 2-hydroxy-2-

methylphenylpropan-1-one. The concentration of acylphosphine oxide initiator in the compositions of the invention may vary depending on the intended use, but is typically in the range 0.1 to 10.0 wt% of the total non-volatiles, preferably 0.5 to 7.5 wt%.

The acylphosphine oxide initiator typically exhibits an absorption maximum in the wavelength range 340 to 400 nm, generally centred at about 380 nm as in the case of Compound (1). However, the molar extinction coefficient is quite low (e.g., about 600 $lmol^{-1}cm^{-1}$ for Compound (1), measured in ethanol solution), so that for the concentration range quoted above, a coated layer of the photocurable composition of the invention of up to 10 μm thickness, which is typical for photoresist applications, has an optical density (OD) of no more than about 0.05 at the photoinitiating wavelength. This means that less than about 10% of the light incident on such a coating would be utilised in photocuring, which is inefficient and leads to severe halation problems in the case of coatings on reflective substrates. The use of higher concentrations of the acylphosphine oxide initiator is undesirable from the point of view of costs and the risk of discoloration due to the tailing of the absorption band into the visible region.

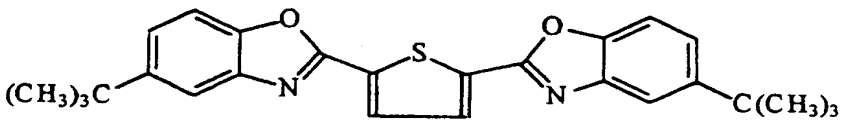
Surprisingly, both aspects of the problem may be solved by incorporating, as a photosensitizer for the acylphosphine oxide initiator, one or more optical brighteners. The optical brighteners in question may be regarded as compounds which have an intense absorption in the near UV region (340 to 400 nm) and which (in the absence of quenchers) fluoresce strongly in the blue region, i.e., at wavelengths above 400nm, typically with a maximum in the range 400 to 450 nm. Suitable compounds are described, as a class, in Kirk-Othmer's Encyclopedia of Chemical Technology, 4th Ed., Vol. 11, pp.227 - 241, and typical examples include stilbene derivatives especially bis(triazinylamino)stilbenes, pyrazolines, bis(benzoxazol-2-yl) derivatives, coumarins, carbostyrils and naphthalimides.

Although many coumarins are known to be powerful optical brighteners, notably those incorporating the 7-amino-4-methylcoumarin nucleus, or the 7-amino-3-phenylcoumarin nucleus, 3-acylcoumarins (in common with other aromatic carbonyl compounds) generally show only a weak fluorescence at most, and are not

normally classed as optical brighteners. Indeed, tests have shown that aromatic carbonyl compounds (including 3-acetylcoumarin) have at best only a moderate sensitising effect on the photolysis of acylphosphine oxides, and hence they do not form part of the present invention.

It has also been found that the acylphosphine oxide quenches the fluorescence of optical brighteners which sensitise its photolysis. This provides a method for screening candidate compounds for sensitising activity. The fluorescence spectrum of the test compound is preferably recorded in a coating in a binder on a suitable substrate with and without the addition of an equimolar amount of the acylphosphine oxide initiator, and the intensity of the emission compared. For the most efficient sensitizers, at least 50% reduction in emission intensity is noted in the presence of the acylphosphine oxide initiator, although essentially any reduction in intensity may be regarded as evidence of potential sensitising activity.

Classes of optical brightener showing high sensitising capability include bis(benzoxazol-2-yl) derivatives, coumarins but not 3-acylcoumarins and pyrazolines, although other factors such as solubility in the appropriate organic media may also influence the choice in any particular situation. A particularly preferred optical brightener is a bis(benzoxazol-2-yl)thiophene derivative supplied by Ciba-Geigy under the trademark Uvitex™ OB having the following structure (3):



(3)

Other commercially available materials useful in the invention include 7-diethylamino-4-methylcoumarin, supplied by Aldrich, Leucopure™ EGM, 7-naphtho-[a]-triazole-3-phenylcoumarin, supplied by Clariant; Hostalux™ KCB, a benzoxazole derivative supplied by Hoechst; and Leucophor™ KNR, a pyrazoline derivative supplied by Clariant.

The quantity of optical brightener in the compositions of the invention is generally in the range 0.1 to 10.0 wt% of the total non-volatiles, but will vary

according to the molar extinction coefficient of the compound(s) involved and the intended use. For example, where photocuring of relatively thick layers is required, a relatively low concentration of optical brightener may be necessary to ensure that the exposing radiation penetrates the full depth. For the photocuring of thinner layers, such as photoresists, higher concentrations may be desirable. In particular, where control of halation in photoimageable systems is important, the concentration should be sufficient to provide an optical density at the exposing wavelength of at least 0.5, preferably at least 1.0.

Although the use of UV absorbers, including optical brighteners, for acutance purposes is known, there is normally a sacrifice of imaging speed. However, because of the unexpected sensitising action of optical brighteners towards acylphosphine oxide initiators, the present invention enables both speed and resolution to be maximised. Furthermore, the optical brightening action enables this to be achieved without the introduction of background coloration.

The sensitizing action of optical brighteners towards acylphosphine oxides is surprising, and difficult to explain on a theoretical basis. While energy transfer from the photoexcited state of fluorescent compounds to a variety of acceptor compounds is known in the literature, theory predicts that this can only occur when the fluorescence spectrum of the energy donor significantly overlaps the absorption spectrum of the acceptor. This is often not the case in the preferred compositions of the invention, where the acylphosphine oxide has an absorption maximum very close to that of the sensitizer, and the fluorescence appears at much longer wavelengths, where the acylphosphine oxide has no detectable absorbance.

Thus, the photosensitization occurring in the compositions of the invention is different from the photosensitization encountered most commonly in the prior art, where the objective is to modify the wavelength response of the initiator, e.g. by moving it from the far UV to the near UV spectral region. In the preferred compositions of the invention, there is no significant change in the wavelength of maximum response, but rather an intensification of the response at the intrinsic sensitivity maximum of the acylphosphine oxide.

The photocurable compositions of the invention further comprise one or more ethylenically unsaturated compounds. Depending on the intended use, any of the unsaturated compounds known in the art of photocurable compositions may be employed, including both polymeric and monomeric species, and mixtures of the two. Thus, in the field of coating, moulding and impregnating compositions, the preferred unsaturated compounds are unsaturated polymeric species such as unsaturated polyesters and polyurethanes as described, for example, in US Patent No. 4,265,723. For photoresist or other imaging applications, lower molecular weight or monomeric species are usually preferred. Suitable monomers are those capable of undergoing photoinitiated chain-growth polymerisation, and include vinyl monomers such as vinyl ethers, vinyl esters, styrenes etc., but the preferred monomers are acrylate or methacrylate esters or amides. Polyfunctional derivatives, possessing two or more polymerizable groups per molecule, are preferred over the monofunctional counterparts, although mixtures of mono- and poly-functional monomers or of different polyfunctional monomers may be used. Particularly preferred monomers include polyacrylates, such as ethylene glycol dimethacrylate, hydantoin hexa-acrylate, trimethylolpropane triacrylate, pentaerythritol tetra-acrylate and the like.

Apart from the three essential ingredients described above, the photocurable compositions of the invention may optionally comprise additional ingredients such as binders, colorants, thickeners, stabilisers, auxiliary initiators, surfactants etc. in accordance with known techniques.

Compositions intended for photoimaging applications preferably contain a binder, the purpose of the binder being to dissolve or disperse the other ingredients and provide the uncured composition with structural integrity. Depending on the type of imaging involved, a wide range of polymers may be used. For example, in photoresists which are subjected to wet processing, a binder adapted for solubility in aqueous (especially alkaline) media may be preferred, incorporating, for example, hydrophilic groups such as carboxylic acid, phenol etc. For other applications, such as peel-apart media, tonable media etc., the binder may be selected on the basis of physical properties such as glass transition temperature (Tg), softening point etc., as is known in the art. The binder is generally selected from thermoplastic polymers such

as polyesters, polycarbonates, polyurethanes, poly(meth)acrylates, cellulose esters and ethers, phenolic resins (including modified versions thereof), poly(vinylalcohol), poly(vinylbutyral), and polymers and copolymers of vinyl monomers such as vinyl chloride, vinyl esters, vinyl ethers, styrene etc.

A binder typically may constitute from about 10 to 80 wt% of the composition, preferably from 25 to 65 wt%.

The photocurable compositions of the invention find use in any application involving the UV-curing of unsaturated monomers or resins, including moulding, impregnating and coating applications as disclosed in US Patent No. 4,265,723, the presence of the optical brightener providing an improvement in sensitivity without yellowing.

The compositions of the invention find particular use in photoimaging systems, where the unique combination of high sensitivity, high resolution and low background color is of prime importance. For some imaging applications, such as the manufacture of printed circuit boards or integrated circuits using microlithographic techniques, the photocurable compositions may be supplied in fluid form, e.g., as a solution or dispersion in an organic solvent, and coated on a surface, such as, copper-clad epoxy laminate, a silicon wafer etc., on which it is desired to perform chemical treatments in selected areas only. After drying, the coating is exposed through a suitable mask, then immersed in a developing solution. The light-exposed (cured) areas resist dissolution in the developer, whereas the unexposed areas are selectively washed away, revealing the underlying surface in those areas which is then available for further chemical treatment.

In the majority of imaging applications, however, the photocurable composition is supplied as a dried coating on a suitable base or substrate.

Therefore, according to a further aspect of the invention, there is provided a photosensitive element comprising a substrate having coated thereon a layer of a photocurable composition comprising one or more ethylenically unsaturated compounds and an acylphosphine oxide initiator, and further comprising, as photosensitizer, an optical brightener. Preferably, the layer of photocurable composition also comprises a binder.

Essentially any substrate of appropriate smoothness and dimensional stability may be coated with the photocurable composition. Rigid substrates, such as glass, may be used, but preferred substrates are flexible, sheet form materials, such as paper, plastic film (particularly polyester film), aluminium foil, etc. An aluminium substrate, preferably subjected to a hydrophilising treatment such as graining, etching, anodising etc., and bearing a coating of the photocurable composition, functions as a negative-acting lithographic printing plate.

The layer of photocurable composition may be releasably attached to a substrate, so that it may be transferred to another surface by a process of lamination followed by peeling of the first substrate. Releasable attachment may be engineered by addition of surfactants, e.g., fluorosurfactants, to the photocurable composition or by surface treatment, e.g., with silicones etc., of the substrate prior to coating the composition on the substrate, as is known in the art. Supplying the photocurable composition as a dried film on a temporary support is frequently more convenient for the end user than supplying it in fluid form.

Photosensitive elements in accordance with the invention are particularly suitable for use in color proofing systems. In the field of halftone full-color printing, it is customary at the prepress stage to assemble a color proof of the image that is intended to be printed. This enables the screened color separations, normally yellow (y), magenta (m), cyan (c) and balancing black (k), to be checked for accuracy and suitability, and provides the customer with a preview of the final image for approval, without the expense of an actual print run. In the normal process, individual photosensitive sheets capable of developing a monochrome image (y, m, c or k) are exposed through contact masks bearing the appropriate color separation image, then developed to form the respective monochrome image, all four images being assembled in register for final viewing. For accurate color reproduction, it is normal practice to assemble the four individual images on a common substrate, without intervening transparent substrates, in the form of a single-sheet (integral) proof, as this provides a close simulation of the printed image.

High resolution and accurate color rendition, with low Dmin, are of fundamental importance in color proofing, but are difficult to achieve in practice.

Since the image comprises four laminated layers, any residual stain caused by the photoinitiating system is multiplied four-fold in the final image. Furthermore, exposure is carried out against a white, diffusely-reflecting base, leading to severe halation effects. The use of photosensitive elements in accordance with the invention allows both these effects to be controlled, without sacrificing imaging speed.

A variety of photomechanical methods are known for the production of integral proofs. In wet-developed systems, such as the Matchprint™ Negative Color Proofing System supplied by Imation Corporation and materials disclosed in patents, such as, US Patent No. 3,671,236, a colored photosensitive imaging element comprising a transparent carrier sheet, a colored photocurable layer and an adhesive layer is laminated (via the adhesive layer) to a suitable base. After removal of the carrier sheet and exposure through the appropriate mask, the assembly is subjected to wet development to selectively remove unexposed areas of the colored layer, producing a negative reproduction of the mask. Thereafter, the entire process is repeated several times, using imaging elements of different colors, until the final image is obtained. By incorporating an acylphosphine oxide initiator and an optical brightener as sensitizer in these proofing elements of the prior art in place of the photoinitiating systems previously employed therein, improvements in sensitivity, resolution and background coloration are obtainable.

Since the need for wet processing is increasingly seen as a disadvantage, various "dry" alternatives have been proposed, including the peel-apart systems disclosed, for example, in EP-A-0601760, WO92/15920, US Patent No. 4,895,787 and many other patents. These systems employ colored photosensitive imaging elements broadly similar in construction to the wet-developed elements described above, but the transparent carrier sheet remains in place during the exposure step. Thereafter, peeling of the carrier sheet results in imagewise partitioning of the colored layer between the carrier sheet and the base, and the entire process is repeated as many times as is necessary, using imaging elements of different colors, to build up the final image on the base. The photoadhesion and photorelease properties of the color layer may be adjusted to leave either a positive or a negative

image on the base. Once again, substitution of a combination of acylphosphine oxide initiator and optical brightener for the conventional photoinitiator can provide improved speed, resolution and Dmin.

Another "dry" method of color proofing is that disclosed in patents such as US Patent No. 3,649,268 and exemplified by the Chromalin™ Proofing System commercially available from Du Pont. In this system, a colorless photocurable layer on a transparent carrier sheet is laminated to a base and exposure is carried out through the carrier sheet, which is then removed. The surface thus revealed bears an imagewise distribution of tacky and non-tacky areas, and this is rendered visible by application of colored toner powder, the toner adhering selectively to the tacky areas. Once again, the entire process is repeated as many times as is necessary to build the complete image, using a toner of different color each time. The colorless photocurable layer is tacky at room temperature in its unexposed state, but photohardens and becomes non-tacky on exposure (i.e. photodetackifies), leading to a positive toned image.

As an alternative to applying toner in powder form, a photodetackified image may be toned by transfer of colorant from a donor sheet, as disclosed, for example in US Patent Nos. 3,620,726; 4,806,451; 5,292,622; 5,372,910; and 5,126,226, and exemplified by the Eurosprint™ Color Proofing System commercially available from Du Pont. In this method, a colorant donor sheet comprising a carrier sheet and a layer of transferable colorant, such as a dispersion of pigment particles in a binder, is laminated to a photodetackified image. On subsequent peeling apart, colorant is transferred preferentially to the tacky areas of the image. In the above-referenced patents and commercial process, the lamination of the colorant donor sheet is invariably carried out at ambient temperature. US Patent No. 4,935,331 discloses a similar proofing process, but with lamination of the colorant donor sheet carried out at elevated temperatures.

The generation of color proofs by methods involving the application of toner to a photodetackified image represents a particularly preferred use for photosensitive elements in accordance with the invention. Therefore, a further aspect of the invention provides a method of imaging comprising the sequential steps of : (a)

providing a photosensitive element comprising a layer of a photocurable composition, as defined above, releasably attached to a transparent carrier sheet; (b) laminating said photosensitive element, via the photocurable layer, to a receiver base; (c) exposing the photocurable layer imagewise to UV light, thereby causing photohardening of the exposed areas of the photocurable layer, said exposure being carried out either before or after removal of the transparent carrier sheet from the photocurable layer; (d) peeling the transparent carrier sheet from the photocurable layer if this has not been carried out in step (c); (e) selectively applying a toner to the non-exposed areas of the photocurable layer; (f) repeating the cycle of steps (a) through (e) at least once, the image-bearing assembly resulting from any cycle becoming the receiver base of step (b) in the succeeding cycle, and a toner of a different color being used in step (e) of each cycle.

In the photosensitive element of step (a), the carrier sheet may comprise any transparent, flexible polymer film of adequate strength for the purpose, but preferably comprises polyester film, e.g., poly(ethylene terephthalate) (PET), with a thickness in the range 5 to 200 μm, preferably 10 to 100 μm. A thinner carrier sheet e.g., 10 to 20 μm, is preferred in situations where exposure is performed through the carrier sheet, but thicker carrier sheets are more easily handled. Optionally, the carrier sheet may be surface-treated to enhance its release properties towards the photosensitive medium.

The photocurable composition comprises a binder, one or more ethylenically-unsaturated monomers, an acylphosphine oxide initiator and an optical brightener as sensitizer as described above, and is typically coated on the carrier sheet as a solution in any of the commonly used organic coating solvents, such as acetone, MEK, THF etc., by conventional techniques such as roller coating, slot coating, bar coating etc. The dry thickness is typically in the range 2 to 12 μm, preferably 4 to 10 μm. The nature and relative proportions of the binder and monomer(s) may be varied to control the physical properties of the layer before and after exposure, e.g., to provide a surface that is tacky at ambient temperature prior to exposure but which hardens to a non-tacky state on photocuring. Alternatively, the layer may be formulated to present a surface which is non-tacky at ambient temperature prior to

exposure, and which softens and tackifies on heating to moderately elevated temperatures, e.g., about 100°C, but which resists such tackification after photocuring. Generally speaking, tackification at low temperatures is favoured by a higher proportion of low molecular weight monomers and/or a lower binder Tg.

Suitable binder materials are colorless, transparent film-forming polymers which are soluble in commonly-used solvents, such as lower alcohols, ketones, ethers, esters, chlorinated hydrocarbons and the like. Examples of suitable binders include acrylic resins, preferred binders comprising poly(methyl methacrylate) (PMMA).

Suitable monomers are those capable of undergoing photoinitiated chain-growth polymerisation, and therefore include vinyl monomers, such as vinyl ethers, vinyl esters, styrenes etc., but the preferred monomers are acrylate or methacrylate esters or amides. Polyfunctional derivatives, possessing two or more polymerizable groups per molecule, are preferred over the monofunctional counterparts, although mixtures of mono- and polyfunctional monomers (or of different polyfunctional monomers) may be used. Highly preferred monomers include ethylene glycol dimethacrylate, hydantoin hexa-acrylate, trimethylolpropane triacrylate, pentaerythritol tetra-acrylate and the like.

In preferred embodiments, which are non-tacky at ambient temperature in the uncured state, the photocurable layer comprises from 40 to 70 wt% PMMA binder, from 20 to 40 wt% monomers, from 1.0 to 10.0 wt% acylphosphine oxide initiator, and from 0.1 to 7.5 wt% optical brightener.

The receiver base (step (b)) provides the background against which the final image is viewed, and hence is preferably selected from white, diffusely-reflecting sheet-form materials. Proofing bases supplied by Imation Corporation under the trademark Matchprint™ are eminently suitable, but essentially any type of paper, plain or coated, may be used if desired. Lamination is most readily carried out by contacting the photocurable layer with the base and passing the assembly through a heated roller device, such as the Matchprint™ laminator. The heat and pressure applied must be sufficient to soften the photocurable layer and cause it to adhere permanently to the receiver base. The amount of heat supplied may be varied by varying the temperature of the rollers and/or their speed of rotation, and may be

optimised for different formulations of the photocurable layer. Using the Matchprint™ laminator, roller temperatures in the range 50 to 150°C are typically found to be suitable.

The next step is the imagewise exposure of the photocurable layer so as to photoharden the light-struck areas. Exposure may be carried out using any of the light sources commonly used for exposing printing plates or proofing elements, such as mercury lamps, metal halide lamps, Xe arc sources etc., and is normally carried out through a photographic mask held in contact with the photocurable layer in a vacuum frame. The mask is normally a color separation positive representing the yellow, magenta, cyan or black content of the final image. The exposure may be performed before or after removal of the carrier sheet of the photosensitive element, but if the surface of the photocurable layer is tacky at ambient temperature, the carrier sheet must be left in position during exposure. When the carrier sheet is removed prior to exposure, it is possible for the photographic mask to contact the photosensitive medium directly, which leads to more accurate image reproduction. On the other hand, if the carrier sheet is left in position during the exposure, it acts as an effective barrier between the photosensitive medium and oxygen of the atmosphere, which otherwise tends to inhibit the photocuring process and hence to increase the exposure time required. In practice, if the carrier sheet is relatively thin (e.g., no more than 50μm in thickness), the loss in resolution caused by exposing through said carrier sheet need not be serious, and the shorter exposing times which result may make this the preferred option.

Following exposure and if necessary, peeling of the carrier sheet, the next step is the application of a toner to adhere selectively to the unexposed (unhardened) areas of the photocurable layer. When the areas are tacky at ambient temperature, toning may be carried out by dusting with a colored powder, as disclosed in US Patent No. 3,649,268, or by transfer of colored toner from a donor sheet, as disclosed in US Patent Nos. 3,620,726; 4,806,451; 5,126,226; 5,292,622; 5,372,910; and 5,427,894.

In preferred embodiments, the unexposed areas of the photocurable layer are non-tacky at ambient temperature, but become tacky when heated to moderately

elevated temperatures. In this case, a colorant donor element is assembled in face-to-face contact with the imagewise photohardened photocurable layer, and the assembly is subjected to heat and pressure to transfer colorant preferentially to the unexposed areas of the photocurable layer. Thereafter, peeling of the colorant donor element reveals a positive monochrome reproduction of the mask used in the exposure step. Once again, the heat and pressure may conveniently be applied using a heated roller device such as the Matchprint™ laminator. The amount of heat supplied must be sufficient to cause softening of the unexposed areas of the photocurable layer and hence causing said areas to adhere strongly to the colorant layer, but must not be so great as to cause softening of the photohardened areas. There is thus a minimum transfer temperature (T_{min}) below which no colorant transfer takes place, and a maximum transfer temperature (T_{max}) above which indiscriminate transfer takes place. The values of T_{max}, T_{min} and (T_{max} - T_{min}) (corresponding to the processing latitude) will vary with the composition of the photocurable layer and the extent of photohardening in the exposed areas. Hence different processing conditions may be required by different formulations or the same formulation exposed under different conditions. For a given formulation of photocurable layer, it may be more convenient to select the processing conditions and vary the exposure conditions to suit.

Having formed a first monochrome image as described above, the entire process is repeated as many times as is necessary to build the full color image, using the image obtained in any one cycle as the receiver base for the succeeding cycle, and using a toner of a different color in each cycle.

Examples

The invention will be illustrated by the Examples in which the following abbreviations trade names are used:

Lucirin™ TPO	acylphosphine oxide photoinitiator supplied by Ciba-Geigy, comprising 100% compound (1)
Irgacure™ 1700	photoinitiator mixture supplied by Ciba-Geigy comprising 25% acylphosphine oxide (2) and 75% 2-hydroxy-2-methylphenylpropan-1-one.

Darocur™ 4265	photoinitiator mixture comprising approx. equal parts acylphosphine oxide (1) and 2-hydroxy-2 methylphenylpropan-1-one, supplied by Ciba-Geigy.
Uvitex™ OB	bis(benzoxazole) optical brightener supplied by Ciba-Geigy (Compound (3)).
Hostalux™ KCB	bis(benzoxazole) optical brightener supplied by Hoechst.
DEMC	7-diethylamino-4-methylcoumarin an optical brightener supplied by Aldrich.
Leucopure™ EGM	7-naphtho-[a]-triazole-3-phenylcoumarin, an optical brightener supplied by Clariant.
Leucophor™ KNR	an optical brightener comprising a cationic pyrazoline derivative in aqueous solution with 2% formic acid, supplied by Clariant.
Blankophor™ MAN-1	an optical brightener comprising a 1,3-diarylpyrazoline, supplied by Bayer.
DPPA	dipentaerythritol penta-acrylate
PETA	pentaerythritol tetra-acrylate
Elvacite™ 2008	poly(methyl methacrylate) supplied by Du Pont.
Joncryl™ 67	styrene/acrylic copolymer resin supplied by SC Johnson Polymer.
Joncryl™ SCX-690	acrylic polymer resin supplied by SC Johnson Polymer.
Butvar™ B76	Polyvinylbutyral, supplied by Monsanto.
MEK	methyl ethyl ketone (butan-2-one)
Dysperbyk™ 161	dispersing agent supplied by BYK-Chemie.
Syloid™ ED50	hydrated silica supplied by Davison Chemical Division.
Cyastat™ SN	quaternary ammonium salt antistat supplied by American Cyanamid.
Catanac™ 609	antistat supplied by American Cyanamid.

PET	untreated poly(ethylene terephthalate) film base.
low-gain/	different grades of Matchprint™ standard base
5	proofing base supplied by Imation Corporation.
Eurosprint™	colorant donor sheet forming part of donor the Eurosprint™ Color Proofing System supplied by Du Pont.

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All laminations were carried out using a Matchprint™ 447 laminator supplied by Imation Corporation. On this apparatus, the temperature of the upper and lower rollers may be varied independently, and the media transport rate is also adjustable. Unless otherwise stated, the lower roller was set at 66°C and the upper roller at
15 132°C, and the transport rate was set at 72 to 75cm/sec.

All exposures were carried out using a 3M Model 7095 printing frame supplied by Minnesota Mining and Manufacturing Company comprising a 3kW metal halide source at a distance of 81cm from the vacuum frame. All dot ranges refer to a 150 line screen.

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Example 1

This Example illustrates the sensitising effect of Uvitex™ OB (Compound 3) on Lucirin™ TPO (Compound 1), and the quenching of the former's fluorescence by the latter. The following basic formulation was prepared:

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Elvacite™ 2008 (20%w/w in MEK)	5.0g
DPPA	0.6g
MEK	1.5g
Disperbyk™ 161	0.043g

To this basic formulation, the following additions were made, to provide formulations F1 (invention), F2 (control) and F3 (control):

	F1	F2	F3
Lucirin™ TPO	0.064g	-	0.064g
Uvitex™ OB	0.013g	0.014g	-

Formulations F1 to F3 were coated on 50 μm PET base at 24 μm wet thickness using a wire-wound bar, then dried for 5 minutes at 85°C. Absorption spectra were measured for the resulting films using a Perkin Elmer Lambda 9 spectrophotometer. For fluorescence measurements, samples of the coatings were laminated to low-gain base, the PET sheet peeled off, and fluorescence measurements made on the transferred coating using a Perkin Elmer MPF-3 fluorescence spectrophotometer equipped with a solid sample holder which held the film at an angle of 45° to the entrance and exit beams. The emission intensity at 435nm was recorded in arbitrary units for excitation at 370 - 380 nm.

For imaging tests, further samples of the coatings were laminated to standard base, and exposed (with the PET sheet still in place) through a test target for varying lengths of time. The target incorporated a step wedge having 0.15 density increments. After peeling off the PET sheet, the exposed samples were laminated with a Eurosprint™ cyan donor, allowed to cool, then peeled apart. Cyan colorant transferred cleanly to those areas which received insufficient exposure to cause photohardening, and so the number of clear steps on the step wedge gave an indication of photosensitivity. The results are summarized in the following table:

	F1	F2	F3
Absorbance (λmax)	0.33 (377nm)	0.32 (377nm)	0.03 (380nm)
Fluorescence (arb. units)	15.3	27.5	0
Steps cleared (12.5 units exp.)	4(5)*	none	(1)*
Steps cleared (20 units exp.)	5(6)*	none	1

* figures in brackets include partially-cleared steps.

These results demonstrate the optical brightener suffers significant fluorescence quenching by the acylphosphine oxide initiator, and the photosensitivity is increased at least four-fold in formulation F1 of the invention.

Example 2

This Example illustrates the effectiveness of a variety of optical brighteners in the practice of the invention. The following control formulation F4 was prepared:

Elvacite™ 2008 (20%w/w in MEK)	5.0g
DPPA	0.65g
Extra Solvent (MEK or toluene)	1.5g
Lucirin™ TPO	0.043g

To the same formulation, the following additions were made, to provide formulations F5 to F8 of the invention:

	F5	F6	F7	F8
Hostalux™ KCB	0.017g	-	-	-
Leucopure™ EGM	-	ca.0.0035g	-	-
DEMC	-	-	0.017g	-
Leucophor™ KNR	-	-	-	0.22g

In F6, the optical brightener was only sparingly soluble, even when toluene was used as the extra solvent. In all other cases, the extra solvent was MEK. For each of F5 to F8, a comparative formulation was prepared in which the Lucirin™ TPO was omitted.

All the formulations were coated and dried as described in Example 1, and absorbance and fluorescence data were recorded as before. For each optical brightener, the fluorescence intensity obtained in the absence of Lucirin™ TPO divided by the fluorescence intensity obtained in its presence gave the Quenching Factor.

Imaging tests were carried out as described previously. The results are summarised in the following table:

	F4	F5	F6	F7	F8
Absorbance (at λ max)	0.02	0.43	0.14	0.44	0.43
Quenching Factor	-	2.5	2.8	2.1	3.9
Steps cleared (12.5 units)	0	2(3)	(1)	1	1(2)
Steps cleared (50 units)	(1)	6(7)	3(4)	5(6)	6(7)

These results demonstrate that all the optical brighteners enhanced the photosensitivity compared to the control coating F4, and all the optical brighteners suffered a quenching of their fluorescence by the acylphosphine oxide initiator.

Example 3

This Example illustrates the use of optical brighteners having a pyrazoline nucleus in the practice of the invention. The following control formulation F9 was prepared:

Elvacite™ 2008 (20%w/w in MEK)	5.0g
DPPA	0.60g
Extra Solvent (MEK)	1.5g
Disperbyk™ 161	0.04g
Lucirin™ TPO	0.064g

To the same formulation, the following additions were made, to provide formulations F10 and F11 of the invention:

F10	Blankophor™ MAN-01	(0.039g)
F11	1,3,5-triphenylpyrazoline	(0.061g)

As before, comparison formulations were prepared using the same quantities of the optical brighteners but lacking the acylphosphine oxide initiator, enabling fluorescence quenching factors to be determined. Absorbance, fluorescence and imaging data were recorded as before, except that an experimental cyan colorant donor sheet was used in place of the Eurosprint™ colorant donor sheet used previously.

The cyan donor sheet was prepared using the following coating formulation:

MEK	836.08g
1-methoxypropan-2-ol	836.08g
Butvar B76	17.136g
Cyan pigment 0061	17.73g
Cyan pigment 1282	16.536g

The formulation was coated on clear PET base to provide a color density of 1.12 measured by reflection with the sheet positioned on a white reflective surface. The following results were obtained:

	F9	F10	F11
Absorbance (at λ max)	0.03	0.71	1.07
Quenching Factor	-	3.6	3.7
Steps cleared (35 units exp.)	nd	1(2)	nd
Steps cleared (40 units exp.)	0	nd	1
Steps cleared (45 units exp.)	nd	2(3)	nd
Steps cleared (80 units exp.)	2(3)	nd	3

nd = not determined

Both pyrazoline derivatives were therefore shown to be effective sensitizers, the 1,3-diaryl derivative (Blankophor™ MAN-01) more so than the 1,3,5-triphenyl derivative. The triphenyl derivative showed an absorbance maximum at a significantly shorter wavelength (358nm) than the diaryl derivative (371nm), and this may relate to the different sensitising properties.

Example 4

This Example illustrates the use of a different acylphosphine oxide initiator in the practice of the invention, namely bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide (compound 2).

Formulations F12 (invention) and F13 and F14 (controls) were prepared as follows:

	F12	F13	F14
Elvacite™ 2008 (20%w/w in MEK)	5.0g	5.0g	5.9g
DPPA	1.0g	1.0g	1.21g
Extra Solvent (MEK)	1.6g	1.6g	1.6g
Disperbyk™ 161	0.05g	0.05g	0.05g
Irgacure™ 1700	0.376g	0.375g	-
Uvitex™ OB	0.075g	-	0.076g

(Irgacure™ 1700 is a mixture comprising 25% Compound (2) and 75% 2-hydroxy-2-methylphenylpropan-1-one.)

The formulations were coated and tested as before, using the colorant transfer sheet of Example 3 in the imaging tests, giving the following results:

	F12	F13	F14
Absorbance (at λ max)	1.72	0.03	1.50
Fluorescence intensity	4.8	-	36
Steps cleared (20 unit exp.)	5(6)	(1)	-
Steps cleared (40 unit exp.)	7(8)	2(3)	-

The results demonstrate that the optical brightener Uvitex OB underwent substantial fluorescence quenching in the presence of Compound (2) and sensitised its photolysis efficiently. In a control experiment, Uvitex™ OB was tested for sensitising action towards 2-hydroxy-2-methylphenylpropan-1-one (in the absence of any acylphosphine oxide initiator), but none was found, nor was any fluorescence quenching observed.

Example 5

This Example demonstrates the utility of the invention in a wet-developed photoresist. A urethane acrylate oligomer in accordance with US Patent No. 4228232 was prepared as follows:

Preparation of Polyol

To a 100ml flask was added 54.3 grams (0.48 equivalents) E-caprolactone, 15.3 grams (0.36 equivalents) dipentaerythritol, and 0.02 grams zinc borate catalyst. The mixture was heated to 170°C for 4 hours under a nitrogen atmosphere. The final hydroxyl equivalent weight was 200.

Preparation of Oligomer

To a 1 litre flask was added 86.2 grams (0.99 equivalents) 2,4-tolylene diisocyanate, 0.61 grams BHT inhibitor, 112 grams methylethyl ketone, 0.12 grams dibutyltin dilaurate catalyst, and 3.5 grams methacrylic acid. A 90/10 nitrogen/oxygen atmosphere was bubbled throughout the reaction. The mixture was stirred and 70.9 grams (0.54 equivalents) hydroxyethyl methacrylate was added slowly.

When all of the hydroxyethyl methacrylate was completely reacted, 175.2 grams (0.91 equivalents) polyol (above), 110 grams of methylethyl ketone, and 0.28 grams dibutyltin dilaurate catalyst are added. The reaction was held at 60°C for 8 hours or until no isocyanate was present by infrared spectroscopy.

Then 27.0 grams (0.27 equivalents) succinic anhydride, 0.7 grams lithium acetate catalyst and 18.0 grams methylethyl ketone were added to the flask. The reaction was held at 70°C for 16 hours. The reaction is complete at this point.

The following formulation was coated at 12 μm wet thickness on clear PET base and dried for 2 minutes at 85°C :

Pigment dispersion	2.00g
Joncryl™ 67 (12.4wt% in MEK)	1.13g
Urethane acrylate (60.0wt% in MEK)	1.00g
Lucirin™ TPO (9.2wt% in MEK)	0.43g
Uvitex™ OB (2.4wt% in MEK)	0.82g

The pigment dispersion comprised Sun 234-0071 red shade magenta pigment (0.50g), Joncryl™ SCX-690 resin (0.50g), Disperbyk™ 161 (0.06g), 1-methoxypropan-2-ol (4.56g) and MEK (4.51g).

A comparison formulation lacking the Uvitex™ OB was coated similarly. Samples of both coatings were exposed (500 units) through a 0.15 increment step wedge as before, then developed in a pH 9.0 buffer solution in order to wash out unpolymerised material. The number of steps retained was as follows:

Invention	8 to 9
Comparison	1 to 2

These results clearly demonstrate the higher sensitivity of the coating in accordance with the invention.

Example 6

This Example demonstrates the utility of the invention in the production of a 4-color proof.

Photosensitive Element

The following formulation was coated as a 16 wt% solids solution in MEK on to 50µm polyester base and dried to give a photocurable layer of dry coating weight 5.3g/m^2 (all quantities are % by weight):

Elvacite™ 2008	55.00
DPPA	32.25
Darocur™ 4265	7.50
Syloid™ ED50	0.50
Dysperbyk™ 161 (30%)	2.00
Uvitex™ OB	0.75
Catanac™ 609 (as solid)	1.00
Cyastat™ SN (as solid)	1.00

Colorant Donor Sheets

Cyan (C), magenta (M), yellow (Y) and black (K) pigment dispersions were prepared by milling the appropriate pigments(s) with Butvar™ B76 in the weight ratio 4:1 in the presence of sufficient solvent (MEK/1-methoxypropan-2-ol 1 : 1 by weight) to provide a solids content of 10 to 12 wt%, then adding the remaining ingredients to the resulting millbases together with further MEK and 1-methoxypropan-2-ol to give a final solids content in the range 3 to 4 wt%. The dispersions were individually roll coated on 50µm PET base sheets to provide a color density of (C) 1.41, (M) 1.37, (Y) 1.31, (K) 1.58 measured by reflection with the sheet positioned on a white reflective surface.

	C	M	Y	K
Butvar™ B76	35.6	35.4	35.4	35.7
Elvacite™ 2008	11.9	11.8	11.8	11.9
Pigment	47.1	47.2	47.2	47.6
Catanac™ 609	2.7	2.8	2.8	2.4
Cyastat™ SN	2.7	2.8	2.8	2.4

Assembly of Proof

A sample of the photosensitive element was assembled with the photocurable layer in contact with standard Matchprint™ base and the assembly passed through the laminator at 80 cm/min. (All subsequent laminations, either of colorant donors or photocurable layers, were carried out at 146 cm/min). After cooling, the assembly was exposed (6 units) through a positive color separation mask representative of the cyan content of an original full color image, causing imagewise photohardening of the photocurable layer. The PET topsheet was removed, a sample of the cyan colorant donor sheet assembled in contact with the imagewise photohardened layer, and the assembly fed through the laminator. After cooling, the colorant donor sheet was peeled away to reveal a positive cyan colored reproduction of the exposure mask. A further sample of the photosensitive element was assembled with the photocurable layer in contact with the cyan image obtained as described above, and the same sequence of steps of repeated, except that exposure (7 units) was through a magenta positive color separation mask and a magenta colorant donor sheet was employed. In this way, the magenta component of the proof was added to the cyan component generated previously. The entire sequence was repeated twice more, employing the appropriate separation masks and colorant donor sheets, to add the yellow and black components of the proof, the exposure being 6 units for the yellow and 5 units for the black. Finally, a uniform exposure of 15 units was carried out to increase the durability of the finished proof.

The resulting proof was of high quality, with no perceptible background staining. The individual color layers were imaged separately through a UGRA test target to test their resolution capabilities, giving the following results:

Cyan	8 microlines, 2 to 99% dots resolved
Magenta	8 microlines, 1 to 99.5% dots resolved
Yellow	10 microlines, 2 to 98% dots resolved
Black	10 microlines, 2 to 99.5% dots resolved

(Dot ranges are for a 150 lines/inch screen).

Example 7

This Example compares the use of optical brighteners with known photosensitizers which are not optical brighteners. The following formulation was prepared at 25 wt% solids in MEK (all quantities are % by weight):

Elvacite™ 2008	47.9
DPPA	40.6
Darocur™ 4265	7.3
Dysperbyk™ 161	2.1
Catanac™ 609	1.0
Cyastat™ SN	1.0

To 10g aliquots of the above were added the following as sensitizers:

(a) none (control)
(b) Blankophor MAN-01 (0.1g) (invention)
(c) 3-Acetylcoumarin (0.1g) (comparison)

Each of the aliquots was coated on polyester base at 5.5g/m^2 (dry) coating weight and dried at 85°C for 5 minutes, stored for 24 hours at room temperature, then laminated to proofing base at 100cm/sec as described previously. Each was given 100 units exposure through a test target incorporating a 0.15 increment step wedge, then toned using the cyan donor sheet of Example 6, after removal of the polyester sheet. The number of clear (untoned) steps gave an indication of photosensitivity, and the results were as follows:

(a) (control) 1 clear step, partially 2
(b) (invention) 4 clear steps, partially 5
(c) (comparison) 0 clear steps, partially 1

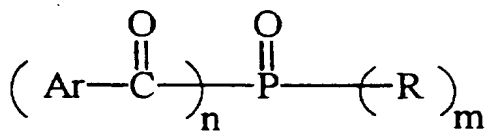
Thus, the comparison compound, 3-acetylcoumarin, showed no discernible sensitising action, and may indeed have exerted a desensitising action.

In a similar experiment, 2-isopropylthioxanthone was tested for sensitising action, and found to increase the photosensitivity relative to the control by a factor of 2, which represents a significantly weaker sensitising action than that of the compounds of the invention. Furthermore, since 2-isopropylthioxanthone is only weakly fluorescent, it cannot be used in high concentrations without imparting an unacceptable yellowing effect.

CLAIMS:

1. A photocurable composition comprising at least one ethylenically unsaturated compound, an acylphosphine oxide initiator, as a photosensitiser, an optical brightener.

2. A photocurable composition as claimed in Claim 1 in which the acylphosphine oxide initiator has the formula:



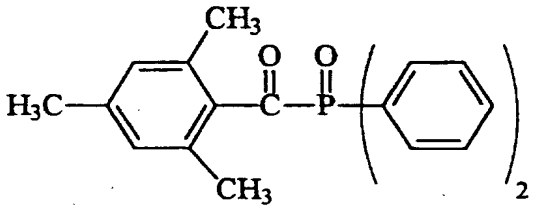
in which:

n and m are 1 or 2 such that (n + m) = 3,

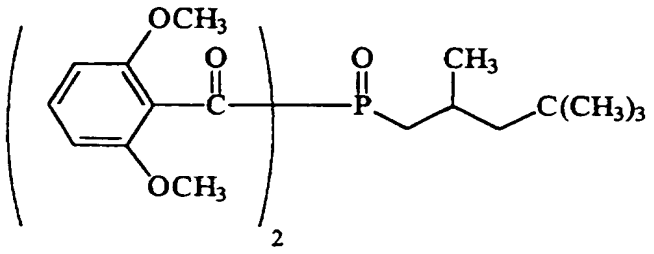
Ar represents an aryl group or heteroaryl group, and

each R is independently selected from alkyl groups, cycloalkyl groups, aryl groups and heterocyclic groups, or when m = 2 both R groups may together complete a cyclic structure comprising atoms selected from C, N, O, S and P.

3. A photocurable composition as claimed in Claim 2 in which the acylphosphine oxide is selected from :



and

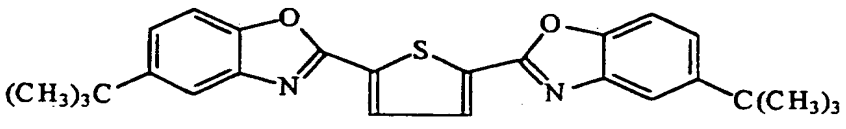


4. A photocurable composition as claimed in any preceding Claim additionally comprising a second initiator selected from benzophenones, acyloins and benzils.

5. A photocurable composition as claimed in any preceding claim in which the concentration of said acylphosphine oxide initiator is in the range 0.1 to 10% by weight of the total involatiles and the optical brightener is present in an amount in the range 0.1 to 10% by weight of said total involatiles.

6. A photocurable composition as claimed in any preceding claim in which the optical brightener is selected from stilbenes, pyrazolines, bis(benzoxazol-2-yl)s, coumarins, carbostyrils and naphthalimides.

7. A photocurable composition as claimed in Claim 8 in which the optical brightener is selected from :



7-diethylamino-4-methylcoumarin, and 7-naphtho-[a]-triazole-3-phenylcoumarin.

8. A photocurable composition as claimed in any preceding Claim in which the optical brightener is present in an amount which provides an optical density of at least 0.5 at the wavelength of the intended exposing radiation.

9. A photocurable composition as claimed in any preceding claim in which the ethylenically unsaturated compound is an unsaturated polyester or unsaturated polyurethane, or a monomer selected from vinyl ethers, vinyl esters, styrenes, acrylate esters, methacrylate esters, acrylate amides and methacrylate amides.

10. A photocurable composition as claimed in Claim 9 in which the ethylenically unsaturated compound comprises a monomer selected from ethylene glycol dimethacrylate, hydantoin hexa-acrylate, trimethylolpropane triacrylate and pentaerythritol tetra-acrylate.

11. A photocurable composition as claimed in any preceding claim which additionally comprises a binder selected from polyesters, polycarbonates, polyurethanes, poly(meth)acrylates, cellulose esters and ethers, phenolic resins, poly(vinyl alcohol), poly(vinylbutyral) and polymers or copolymers of vinyl chloride, vinyl esters, vinyl ethers styrene and mixtures thereof, said binder being present in an amount of from 10 to 80% by weight of total involatiles.

12 A photosensitive element comprising a substrate bearing a layer of a composition as claimed in any preceding claim.

13. A photosensitive element as claimed in Claim 12 comprising a transparent substrate, a coloured layer of said composition and an adhesive layer.

14. A photosensitive element as claimed in Claim 12 comprising a transparent substrate and said layer wherein said layer is tacky in its unexposed state but photohardens and becomes non-tacky on exposure.

15 A photosensitive element as claimed in Claim 14 in which said layer is non-tacky at room temperature but tacky at elevated temperatures in its non-exposed state.

16. A use of an optical brightener as a photosensitiser for an acylphosphine initiator..

17. A method of photocuring which comprises exposing a composition as claimed in any one of Claims 1 to 11 or an element as claimed in any one of Claims 12 to 15 to radiation having a wavelength in the range 340 to 400nm.

18. A method of imaging comprising image-wise exposing a photosensitive element as claimed in any one of Claims 12 to 15 to radiation having a wavelength in the range 340 to 400nm.

19. A method of imaging comprising the sequential steps of:

(a) providing a photosensitive element as claimed in Claim 14 or Claim 15 having a transparent substrate,

(b) laminating said photosensitive element, via the photocurable layer, to a receiver base,

(c) exposing the photocurable layer imagewise to UV light, thereby causing photohardening of the exposed areas of the photocurable layer, said exposure being carried out either before or after removal of the transparent substrate from the photocurable layer,

(d) peeling the transparent substrate from the photocurable layer if this has not be carried out in step (c),

(e) selectively applying a toner to the non-exposed areas of the photocurable layer,

(f) repeating the cycle of steps (a) through (e) at least once, the image-bearing assembly resulting from any cycle becoming the receiver base of step (b), and a toner of different colour being used in step (e) of each cycle.

INTERNATIONAL SEARCH REPORT

Int ional Application No
PCT/US 97/04569

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G03F7/029 G03F3/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 292 740 A (CIBA-GEIGY AG) 6 March 1996 see page 22, line 30 - page 23, line 5; example 34 see page 21, line 18-21 ---	1-6,8-19
X	GB 2 259 704 A (CIBA-GEIGY AG) 24 March 1993 see page 6, line 1; claim 1; examples 9,45 see page 7, line 28-32 ---	1-6,8-19
X,Y	US 5 425 970 A (E. LAHRMANN ET AL.) 20 June 1995 see column 5, line 30-34 see column 7, line 46-56 --- -/--	1-6,8-19

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
28 July 1997	11.08.97
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Authorized officer Thiele, N

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Int ional Application No
PCT/US 97/04569

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 057 474 A (BASF AG) 11 August 1982 see page 9, line 1-8; claim 7; examples 6-11	1-6,8-19
A	DE 31 33 419 A (BASF AG) 10 March 1983 Table 2	1-19
A	EP 0 412 495 A (E.I. DU PONT DE NEMOURS AND COMPANY) 13 February 1991 see page 7, line 48-54	1-19
X,P	EP 0 741 331 A (BAYER CORPORATION) 6 November 1996 see claim 5; example 2	1-19
X,P	EP 0 741 333 A (BAYER CORPORATION) 6 November 1996 see claims 1,11; examples 1,3,7	1-19
X,P	EP 0 718 694 A (JAPAN SYNTHETIC RUBBER CO.) 26 June 1996 see claims 1,18	1-19

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int ional Application No
PCT/US 97/04569

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2292740 A	06-03-96	AT 402298 B	25-03-97
		AT 147195 A	15-08-96
		AU 3028695 A	09-05-96
		BR 9503915 A	17-09-96
		CN 1130632 A	11-09-96
		CZ 9502236 A	13-03-96
		DE 19532358 A	07-03-96
		FR 2724172 A	08-03-96
		JP 8081481 A	26-03-96
		NL 1001124 A	04-03-96
		SE 9503022 A	03-03-96
		SG 28300 A	01-04-96
		ZA 9507404 A	17-04-96
GB 2259704 A	24-03-93	CH 682666 A	29-10-93
		AT 401265 B	25-07-96
		AT 188592 A	15-12-95
		AU 655675 B	05-01-95
		AU 2525192 A	01-04-93
		BE 1006011 A	19-04-94
		CA 2078722 A	24-03-93
		DE 4231579 A	25-03-93
		ES 2050607 A	16-05-94
		FR 2681599 A	26-03-93
		IT 1255509 B	09-11-95
		JP 5345790 A	27-12-93
		NL 9201641 A	16-04-93
		SE 503060 C	18-03-96
		SE 9202668 A	24-03-93
		US 5472992 A	05-12-95
		US 5399770 A	21-03-95
		ZA 9207226 A	23-03-93
US 5425970 A	20-06-95	DE 4215070 A	11-11-93
		EP 0568967 A	10-11-93
		JP 6063494 A	08-03-94
EP 57474 A	11-08-82	DE 2909994 A	02-10-80
		CA 1129422 A	10-08-82
		DK 171353 B	16-09-96

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inv ional Application No
PCT/US 97/04569

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 57474 A		EP 0007508 A	06-02-80
		US 4298738 A	03-11-81
		US 4710523 A	01-12-87
DE 3133419 A	10-03-83	CA 1200559 A	11-02-86
		EP 0073413 A	09-03-83
		JP 1772154 C	14-07-93
		JP 4057677 B	14-09-92
		JP 58077890 A	11-05-83
		US 4447520 A	08-05-84
EP 412495 A	13-02-91	US 4987051 A	22-01-91
		AU 631672 B	03-12-92
		AU 6025690 A	14-02-91
		CA 2022627 A	10-02-91
		CN 1051435 A	15-05-91
		JP 3089249 A	15-04-91
EP 741331 A	06-11-96	AU 5071696 A	14-11-96
		CA 2174294 A	06-11-96
		JP 8305004 A	22-11-96
EP 741333 A	06-11-96	AU 5071796 A	14-11-96
		CA 2175759 A	06-11-96
		JP 8305018 A	22-11-96
EP 718694 A	26-06-96	JP 8171209 A	02-07-96